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THE THOMSON EFFECT AND THERMAL CONDUCTION IN METALS

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The Thomson Effect.—In these PROCEEDINGS for March, 1920, is a paper in which I undertook to account for the Thomson effect values, as found by Bridgman for many metals, in accordance with the hypothesis of dual electric conduction.

Using data obtained by the methods of that paper, I was able, as I stated at the Washington meeting of the National Academy in April, 1920, to account quantitatively for the values of thermal conductivity found in a large number of metals at room temperature. I stated further, however, that the temperature-coefficient of thermal conductivity indicated by my calculations was far too large to accord with the obvious facts, and that a revision of my formulae was therefore necessary. This revision, which has now been made, enables me to deal pretty satisfactorily with thermal conduction, if my assumptions are granted. It involves important changes in most of the numerical tables in the paper referred to, but no great change in the method there followed.

The revision begins with equation (11), which is changed by the substitution of s for 2.5, so that it now stands

$$\lambda' = \lambda'_0 + sRT, \quad (1)$$

where s is a constant, which varies from one metal to another but is always greater than 2.5. The λ' of this equation is the number of ergs required to separate one electron from its atomic union and leave it free, as a gas particle, within a metal; λ'_0 is a constant which may be different in different metals, and R is the gas constant for a single molecule. The assumption involved in this equation, like some others I have made, may seem improbable; but, as it does not, so far as I am aware, conflict with established facts or principles,¹ and as it serves my purpose fairly well, I have felt justified in adopting it provisionally.

As the total energy which a free electron possesses in virtue of its character as a monatomic gas molecule is $2.5 RT$, the kinetic energy and the pv energy being taken together, and as I assume that this energy is acquired in the act of ionization, I have

$$\lambda' = 2.5 RT, \text{ or } \lambda'_0 + (s - 2.5)RT,$$

as the number of ergs required for overcoming the attractions or repulsions which are operative in the act of freeing a single electron from an atom, under the conditions which prevail within a solid metal. The

supposed increase of this quantity with rise of temperature may be due to the expansion of the metal.

The meaning of P_a and P_f , symbols which I have used before and shall presently use again, is such that

$$P_f - P_a = \frac{1}{e} (\lambda'_0 + (s - 2.5)RT), \quad (2)$$

where e is the electron charge.

The revision leaves equations (12), (13), (17) of my previous paper unchanged, but in (14) it substitutes $(s + 1.5 - q)$ for $(4 - q)$ in the first term of the second member, and in (15) it puts $(2s + 1.5 - q)$ in place of $(6.5 - q)$.

Thermal Conduction.—In December, 1917, I proposed² the following theory: That thermal conduction in a metal is due to the convective action of a circulating electric current, free electrons moving down the temperature gradient and associated electrons moving up, with ionization at the hot part of the metal, involving absorption of heat, and re-association at the cold end, involving the emission of heat. I now propose to go as far as I can at present in the way of submitting this theory to a quantitative test.

As in my previous papers, "hypothesis (A)" will mean the assumption that the purely mechanical tendency of the free-electron gas is toward equality of pressure throughout the metal. Under this hypothesis the condition of equilibrium in a detached metal bar having an established and permanent temperature gradient is expressed by the equation

$$k_f \left(\frac{1}{ne} \frac{dp}{dl} + \frac{dP}{dl} + \frac{dP_f}{dl} \right) = -k_a \left(\frac{dP}{dl} + \frac{dP_a}{dl} \right). \quad (3)$$

This comes from equation (1) of my paper in these Proceedings for April, 1918, by substitution for μ according to equation (2) of that paper, which *should be*

$$\mu = k_f \frac{I}{Cne^2}.$$

The first member of (3) as just given is the strength of the free-electron current, down the temperature gradient, and the second member is the strength of the associated-electron current, up the temperature gradient, per unit cross-section of the bar. We can rewrite (3) as follows, taking, for simplicity, the case in which $(dT \div dl) = 1$:

$$k_f \left(\frac{1}{ne} \frac{dp}{dT} + \frac{dP}{dT} + \frac{dP_f}{dT} \right) = -k_a \left(\frac{dP}{dT} + \frac{dP_a}{dT} \right). \quad (4)$$

The term $(dP_f \div dT)$ expresses a possible differential attraction of the unequally heated metal for the free electrons, tending to move them down the temperature gradient, something distinct from the force due to the gradient of potential $(dP \div dT)$, which the gas-pressure drift

of the free electrons produces. The term $(dP_a \div dT)$ has a corresponding meaning with regard to the associated electrons.

The relation between P_f and P_a being expressed by equation (2), we must suppose at least one of the ratios $(dP_f \div dT)$ and $(dP_a \div dT)$ to have a finite value. I shall assume the value of $(dP_a \div dT)$ to be negligible, and therefore we shall have, from equation (2),

$$\frac{dP_f}{dT} = \frac{R}{e} \cdot (s - 2.5). \quad (5)$$

Since

$$p = nRT, \quad (6)$$

and, according to a previous assumption,

$$n = zT^q, \quad (7)$$

where z and q are constants, we have

$$\frac{1}{n} \frac{dp}{dT} = R \left(1 + \frac{T}{dT} \frac{dn}{n} \right) = R(1 + q). \quad (8)$$

Substituting from (5) and (8) in (4) and taking $(dP_a \div dT)$ as zero, we get

$$k_f \left(\frac{R}{e} (s + q - 1.5) + \frac{dP}{dT} \right) = -k_a \frac{dP}{dT}. \quad (9)$$

According to my conception of thermal conduction, we have only to multiply either side of this equation by λ , the amount of energy required to free $(1 \div e)$ electrons within the metal, to get the value of θ , the thermal conductivity of the metal. That is, we can write

$$\theta = -\lambda k_a \frac{dP}{dT} \text{ ergs/cm., sec., deg. C.} \quad (10)$$

We must now deal with the individual factors in the second member of this equation. From (9), remembering that $k = k_a + k_f$, we get

$$\frac{dP}{dT} = -\frac{R}{e} \frac{k_f}{k} (s + q - 1.5), \quad (11)$$

and λ is $(1 \div e)$ times the λ' of equation (1).

Hence we have

$$\theta = \frac{R^2}{e^2} \left(\frac{\lambda'_0}{R} + sT \right) k_a \frac{k_f}{k} (s + q - 1.5). \quad (12)$$

Of course, since k is known, k_a is known if k_f is known. Substantially, my method of procedure with each metal is to find by trial values of λ'_0 , s , $(k_f \div k)$, and q , that will in combination account for Bridgman's value of σ , the Thomson effect, and then from the many combinations that will do this to find the smaller number that will account also for the known value of θ . Ultimately I must undertake to find from the combinations that meet these two tests the ones that will account for or be consistent with the Peltier effect, but I shall not do that in this paper.

In the following tables, as in the corresponding tables of my March paper, the metals are divided into four groups, according to their values of K_1 and K_2 in the equation $\sigma = (K_1 + K_2 t)T$. Two alloys also, constantan and manganin, are dealt with according to the data given for them by Bridgman. In finding k_{100} , the electrical conductivity at 100° C., from k_0 , the conductivity at 0° C., I have used Bridgman's temperature coefficients; but he, working with very fine wires, did not determine the absolute conductivity at any temperature. The values of θ_0 and θ_{100} given in the first line beneath the name of any metal are derived from the work of Jaeger and Diesselhorst, except in those cases where a footnote is referred to. They are expressed in cal./cm., sec., deg. C. C , C_1 and C_2 are constants in the equation

$$(K_f \div K) = C + C_1 t + C_2 t^2.$$

The δ_c of these tables is the constant part of the "ionizing potential," expressed in volts; δ_0 ³ is the total ionizing potential at 0° C., and δ_{100} is the total ionizing potential at 100° C.

The letter γ indicates the estimated percentage of atoms which are ionized at 0° C. The method of estimation is given later.

First Group: Metals for which $K_1 > 0$ and $K_2 = 0$.

TABLE 1: COBALT

$$k_0 = 102 \times 10^{-6}; k_{100} = 74.7 \times 10^{-6}; \theta_0 = 0.161; \theta_{100} = 0.164; (\theta_0 \div \theta_{100}) = \lambda.098$$

$$\sigma = 7.8 \text{ T ergs/deg. C.}$$

$$\text{If } q = 1.55 \text{ and } s = 4 \text{ and } \lambda'_0 = 42 \text{ R, } C_1 = 230 \times 10^{-6} \text{ and } C = 0.256$$

$\left(\frac{k_f}{k}\right)_{100}$	γ	δ_c	δ_0	δ_{100}	$\left(\frac{dP}{dT}\right)_0$	$\left(\frac{dP}{dT}\right)_{100}$	$(ka)_0 \times 10^6$	$(ka)_{100} \times 10^6$	θ_0	θ_{100}	$\frac{\theta_0}{\theta_{100}}$
0.279	6.7%	0.004	0.098	0.132	-8920	-9720	76.0	54.0	0.157	0.165	0.95

¹ Lacking observed values of θ_0 and θ_{100} for cobalt, I have estimated the values here given by use of the Wiedemann-Franz ratio (average for 13 metals) applied to k_0 and k_{100} .

TABLE 2: NICKEL

$$k_0 = 93 \times 10^{-6}; k_{100} = 62.5 \times 10^{-6}; \theta_0 = 0.143; \theta_{100} = 0.138; (\theta_0 \div \theta) = 1.04$$

$$\sigma = 3.56 \text{ T ergs/deg. C.}$$

$$\text{If } q = 1.55 \text{ and } s = 4 \text{ and } \lambda'_0 = 100 \text{ R, } C_1 = 105 \times 10^{-6} \text{ and } C = 0.239$$

$\left(\frac{k_f}{k}\right)_{100}$	γ	δ_c	δ_0	δ_{100}	$\left(\frac{dP}{dT}\right)_0$	$\left(\frac{dP}{dT}\right)_{100}$	$(ka)_0 \times 10^6$	$(ka)_{100} \times 10^6$	θ_0	θ_{100}	$\frac{\theta_0}{\theta_{100}}$
0.250	5.7%	0.009	0.103	0.137	-8330	-8710	70.8	46.9	0.144	0.133	1.08

TABLE 3: PALLADIUM

$$k_0 = 100 \times 10^{-6}; k_{100} = 75.9 \times 10^{-6}; \theta_0 = 0.165; \theta_{100} = 0.182; (\theta_0 \div \theta_{100}) = 0.91$$

$$\sigma = 3.52 \text{ T ergs/deg. C.}$$

$$\text{If } q = 1.6 \text{ and } s = 6 \text{ and } \lambda'_0 = 114 \text{ R, } C_1 = 69.8 \times 10^{-6} \text{ and } C = 0.0987$$

$\left(\frac{k_f}{k}\right)_{100}$	γ	δ_c	δ_0	δ_{100}	$\left(\frac{dP}{dT}\right)_0$	$\left(\frac{dP}{dT}\right)_{100}$	$(ka)_0 \times 10^6$	$(ka)_{100} \times 10^6$	θ_0	θ_{100}	$\frac{\theta_0}{\theta_{100}}$
0.106	3.2%	0.010	0.151	0.203	-5180	-5550	90.1	67.9	0.168	0.182	0.92

TABLE 4: PLATINUM

$k_o = 110 \times 10^{-6}$; $k_{100} = 79.3 \times 10^{-6}$; $\theta_o = 0.163$; $\theta_{100} = 0.173$; $(\theta_o \div \theta_{100}) = 0.95$
 $\sigma = 2.67 T$ ergs/deg. C.

If $q = 1.6$ and $s = 7$ and $\lambda'_o = 117 R$, $C_1 = 45.2 \times 10^{-6}$ and $C = 0.0652$

$\left(\frac{k_f}{k}\right)_{100}$	γ	δ_c	δ_o	δ_{100}	$\left(\frac{dP}{dT}\right)_o$	$\left(\frac{dP}{dT}\right)_{100}$	$\frac{(ka)_o}{\times 10^6}$	$\frac{(ka)_{100}}{\times 10^6}$	θ_o	θ_{100}	$\frac{\theta_o}{\theta_{100}}$
0.070	2.3%	0.01	0.174	0.235	-3980	-4260	103	74	0.170	0.175	0.97

TABLE 5: TIN

$k_o = 105 \times 10^{-6}$; $k_{100} = 72.6 \times 10^{-6}$; $\theta_o = 0.157$; $\theta_{100} = 0.145$; $(\theta_o \div \theta_{100}) = 1.08$
 $\sigma = 0.134 T$ ergs/deg. C.

If $q = 1.51$ and $s = 8$ and $\lambda'_o = 234 R$, $C_1 = 1.97 \times 10^{-6}$ and $C = 0.0466$

0.047	2.3%	0.02	0.208	0.277	-3210	-3220	100	69.2	0.159	0.147	1.08
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TABLE 6: ZINC

$k_o = 180 \times 10^{-6}$; $k_{100} = 127 \times 10^{-6}$; $\theta_o = 0.266$; $\theta_{100} = 0.262$; $(\theta_o \div \theta_{100}) = 1.02$
 $\sigma = 0.99 T$ ergs/deg. C.

If $q = 1.55$ and $s = 10$ and $\lambda'_o = 117 R$, $C_1 = 11.64 \times 10^{-6}$ and $C = 0.0304$

0.032	1.6%	0.01	0.245	0.331	-2630	-2730	175	123	0.268	0.265	1.01
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Second Group: Metals for which $K_1 < 0$ and $K_2 = 0$.

TABLE 7: BISMUTH

$k_o = 9.3 \times 10^{-6}$; $k_{100} = 646 \times 10^{-6}$; $\theta_o = 0.0201$; $\theta_{100} = 0.0161$; $(\theta_o \div \theta_{100}) = 1.25$
 $\sigma = -3.2 T$ ergs/deg. C.

If $q = 1.25$ and $s = 2.8$ and $\lambda'_o = 1170 R$, $C_1 = -122.6 \times 10^{-6}$ and $C = 0.540$

0.528	2.9%	0.10	0.166	0.190	-11800	-11600	4.28	3.05	0.0200	0.0160	1.25
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CADMIUM

$k_o = 160 \times 10^{-6}$; $k_{100} = 112.4 \times 10^{-6}$; $\theta_o = 0.223$; $\theta_{100} = 0.216$; $(\theta_o \div \theta_{100}) = 1.03$
 $\sigma = -32.4 T$ ergs/deg. C.

It is easy to find values of q , s and λ'_o that will give the right value for θ_o ; but the value of θ_{100} that results is much too small. I cannot deal satisfactorily with cadmium at present, owing to the very large negative value that Bridgman finds for its σ , a value which is about ten times as great as those deducible from the work of various other investigators who have studied the thermo-electric behavior of this metal. See, for example, a paper by Dewar and Fleming, *Phil. Mag.*, Vol. 40, 5th Series, 1895. It is possible that Bridgman has made some mistake in this case.

TABLE 8: COPPER

$k_o = 650 \times 10^{-6}$; $k_{100} = 455 \times 10^{-6}$; $\theta_o = 0.920$; $\theta_{100} = 0.908$; $(\theta_o \div \theta_{100}) = 1.01$
 $\sigma = -0.966$ T ergs/deg. C.

If $q = 1.49$ and $s = 9$ and $\lambda'_o = 3.24$ R, $C_1 = -12.54 \times 10^{-6}$ and $C = 0.0372$

$\left(\frac{k_f}{k}\right)_{100}$	γ	δ_c	δ_o	δ_{100}	$\left(\frac{dP}{dT}\right)_o$	$\left(\frac{dP}{dT}\right)_{100}$	$(k_a)_o \times 10^6$	$(k_a)_{100} \times 10^6$	θ_o	θ_{100}	$\frac{\theta_o}{\theta_{100}}$
0.036	6.4%	0.003	0.214	0.292	-2880	-2780	626	439	0.918	0.850	1.08

TABLE 9: MAGNESIUM

$k_o = 240 \times 10^{-6}$; $k_{100} = ?$; mean θ between 0° and $100^\circ = 0.376$

$\sigma = -0.008$ T ergs/deg. C.

If $q = 1.499$ and $s = 6.5$ and $\lambda'_o = 460$ R, $C_1 = -14.4 \times 10^{-8}$ and $C = 0.066$

0.066	12%	0.039	0.192	0.248	-3700	-3700	224	?	0.379	?	?
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TABLE 10: SILVER

$k_o = 670 \times 10^{-6}$; $k_{100} = 476 \times 10^{-6}$; $\theta_o = 1.01$; $\theta_{100} = 0.99$; $(\theta_o \div \theta_{100}) = 1.02$

$\sigma = -0.864$ T ergs/deg. C.

If $q = 1.49$ and $s = 11.5$ and $\lambda'_o = 30$ R, $C_1 = -8.8 \times 10^{-6}$ and $C = 0.0240$

0.023	5.5%	0.003	0.272	0.370	-2380	-2280	655	466	1.01	0.94	1.08
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TABLE 11: TUNGSTEN

$k_o = 140 \times 10^{-6}$; $k_{100} = 106 \times 10^{-6}$; $\theta_{18} = 0.35$; $\theta_{100} = ?$

$\sigma = -3.41$ T ergs/deg. C.

If $q = 1.49$ and $s = 9$ and $\lambda'_o = 18.4$ R, $C_1 = -44.4 \times 10^{-6}$ and $C = 0.0696$

0.065	3.2%	0.002	0.213	0.290	-5380	-5030	130	99	0.355	0.344	1.03
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¹ Value found by Coolidge.

Third Group: Metals for which $K_1 > 0$ and $K_2 > 0$.

TABLE 12: IRON

$k_o = 78 \times 10^{-6}$; $k_{100} = 48 \times 10^{-6}$; $\theta_o = 0.163$; $\theta_{100} = 0.151$; $(\theta_o \div \theta_{100}) = 1.08$

$\sigma = (1.78 T + 6.04 tT)$ ergs/deg. C.

If $q = 1.205$ and $s = 11$ and $\lambda'_o = 117$ R, $C_2 = 26.9 \times 10^{-8}$, $C_1 = 14.8 \times 10^{-6}$,
 $C = 0.0364$

0.041	1.2%	0.01	0.268	0.363	-3350	-3740	75.2	46.2	0.161	0.149	1.08
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TABLE 13: THALLIUM

$k_o = 57 \times 10^{-6}$; $k_{100} = 43.9 \times 10^{-6}$; $\theta_o = 0.090(?)$; $\theta_{100} = 0.096(?)$; $(\theta_o \div \theta_{100}) = 0.94(?)$

$\sigma = (0.268 T \times 0.00336 tT)$ ergs/deg. C.

If $q = 1.48$ and $s = 7$ and $\lambda'_o = 117$ R, $C_2 = 2.80 \times 10^{-4}$, $C_1 = 3.56 \times 12^{-6}$, $C = 0.0676$

0.068	1.9%	0.01	0.174	0.236	-4060	-4100	53.1	41.0	0.089	0.094	0.95
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¹ See footnote under table 1, cobalt.

TABLE 14: ALUMINIUM

Fourth Group: Metals for which $K_1 < 0$ and $K_2 > 0$ $k_o = 380 \times 10^{-6}$; $k_{100} = 265 \times 10^{-6}$; $\theta^\circ = 0.477$; $\theta_{100} = 0.492$; $(\theta^\circ \div \theta_{100}) = 0.97^1$ $\sigma = (-0.016 T + 0.006 tT)$ ergs/deg. C.If $q = 1.45$ and $s = 5.5$ and $\lambda'_o = 125 R$, $C_2 = 6.35 \times 10^{-8}$, $C_1 = -3.04 \times 10^{-4}$,
 $C = 0.0886$

$\left(\frac{k_f}{k}\right)_{100}$	γ	δ_c	δ_o	θ_{100}	$\left(\frac{dP}{dT}\right)_o$	$\left(\frac{dP}{dT}\right)_{100}$	$\frac{(k_a)_o}{\times 10^6}$	$\frac{(k_a)_{100}}{\times 10^6}$	θ_o	θ_{100}	$\frac{\theta_o}{\theta_{100}}$
0.089	11%	0.011	0.140	0.187	-4150	-4170	346	241	0.479	0.449	1.07

¹ Lees found $\theta_{18} = 0.524$ in this metal; but apparently he did not determine θ_{100} .

TABLE 15: GOLD

 $k_o = 490 \times 10^{-6}$; $k_{100} = 351 \times 10^{-6}$; $\theta_o = 0.699$; $\theta_{100} = 0.703$; $(\theta_o \div \theta_{100}) = 0.994$ $\sigma = (-0.934 T + 0.001 tT)$ If $q = 1.495$ and $s = 8$ and $\lambda'_o = 15 R$, $C_2 = 0.73 \times 10^{-8}$, $C_1 = -13.7 \times 10^{-8}$, $C = 0.0486$

0.047	8%	0.002	0.190	0.259	-3340	-3290	466	335	0.705	0.672	1.05
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TABLE 16: MOLYBDENUM

 $k_o = 274 \times 10^{-6}$; $k_{100} = 191 \times 10^{-6}$; $\theta_o = 0.43(?)$; $\theta_{100} = 0.42(?)$; $(\theta_o \div \theta_{100}) = 1.02(?)$ $\sigma = (-4.33 T + 0.015 tT)$ ergs/deg. C.If $q = 1.3$ and $s = 10$ and $\lambda'_o = 110 R$, $C_2 = 8.7 \times 10^{-8}$, $C_1 = -51 \times 10^{-8}$, $C = 0.0338$

0.0296	2.8%	0.009	0.244	0.330	-2850	-2490	265	185	0.439	0.363	1.21
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¹ See footnote under table 1, cobalt.

ALLOYS

TABLE 17: CONSTANTAN

 $k_o = 20.4 \times 10^{-6}$; $k_{100} = 20.4 \times 10^{-6}$; $\theta_o = 0.052$; $\theta_{100} = 0.064$; $(\theta_o \div \theta_{100}) = 0.81$ $\sigma = 7.94 T$ ergs/deg. C.If $q = 1.55$ and $s = 5$ and $\lambda'_o = 90 R$, $C_1 = 188 \times 10^{-6}$ and $C = 0.288$

0.306 ¹	1%	0.008	0.126	0.169	-12500	-13300	14.5	14.2	0.054	0.076	0.71
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¹ Very roughly estimated from the values of γ given for copper and nickel.

TABLE 18: MANGANIN

 $k_o = 23.8 \times 10^{-6}$; $k_{100} = 23.8 \times 10^{-6}$; $\theta_o = 0.051$; $\theta_{100} = 0.063$; $(\theta_o \div \theta_{100}) = 0.81$ $\sigma = (-0.828 T - 0.00672 tT)$ ergs/deg. C.If $q = 1.51$ and $s = 4.5$ and $\lambda'_o = 90 R$, $C_2 = -8.74 \times 10^{-8}$, $C_1 = -18.0 \times 10^{-8}$
 $C = 0.27$

0.267	1% ¹	0.008	0.113	0.152	-10500	-10400	17.4	17.5	0.049	0.066	0.75
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¹ See footnote under table 17.

Comments.—There is a curious tenacity in the value of $(\theta_0 \div \theta_{100})$ for any metal, as found by the method of this paper. Thus in no case except that of Co, where a great range of $(k_f \div k)$ was tried, did the value of $(\theta_0 \div \theta_{100})$ change from >1 to <1 with any variations of q , s and λ'_0 . Out of seventeen cases, including those of constantin and manganin, the value of $(\theta_0 \div \theta_{100})$, as found by experiment or calculated by the use of the Wiedemann-Franz ratio, is in nine greater than 1 and in eight less than 1. In only two of these cases, those of aluminium and gold, does the method of this paper fail to give a value of $(\theta_0 \div \theta_{100})$ on the right side of 1.

In nine of these seventeen cases, Bi, Co, Fe, Ni, Pd, Pt, Sn, Tl, Zn, it has been found practicable to get a combination of q , s and λ'_0 that will account for Bridgman's σ and give the desired values of both θ_0 and θ_{100} to any reasonable degree of accuracy. In all of these nine cases, except that of Bi, the value of K_1 in the equation $\sigma = K_1 T + K_2 tT$ is positive.

In six of the other eight cases the value of $(\theta_0 \div \theta_{100})$ here found is larger than the one found by experiment or indicated by the *W-F* rule. In four cases, Ag, Al, Au, Cu, the discrepancy is about 6–10%; in one, that of Mo, it may be considerably greater, but this is a *W-F* case; in only one, that of Cd, is the disagreement hopelessly great. In constantin and in manganin the calculated $(\theta_0 \div \theta_{100})$ is less than the observed.

The value of γ , the percentage of ionized atoms within a metal, has been estimated by means of the formula¹

$$k_f = \frac{n c l e^2}{4 R T}.$$

When T is taken as 273, we have, approximately,

$$k_f = 1.91 \times 10^{-20} n l = 1.91 \times 10^{-20} \gamma \nu l,$$

or

$$\gamma = 5.24 \times 10^{-19} (k_f \div \nu l),$$

where ν is the number of atoms of the metal per cu. cm. and l is the length of the "mean free path" of the electrons among the atoms.

Concerning the value of l , I have been and am still much in doubt. Adams and Chapman, in a study of the Corbino effect,⁴ estimated it to be in copper not far from 3×10^{-7} cm., which is about 13 times the distance from centre to centre of adjacent atoms, if a cubical arrangement of the atoms is assumed. Compton, K. T., and Ross⁵ concluded that a photo-electrically excited electron may move about 2.67×10^{-7} cm. in platinum, about 11 times the centre to centre distance of the atoms, and approximately 5×10^{-7} cm. in gold, nearly 20 times the atomic distance. I have taken l as 10 times the atomic distance, thus putting $l = (10 \div \nu_3^{\frac{1}{3}})$ and making

$$\gamma = 0.52 \times 10^{19} \times k_f \div \nu_3^2.$$

A much smaller estimate of l than the one I have used would be disastrous for my speculations, as it would give large values of γ and thus in-

introduce an insuperable difficulty regarding specific heat. Even with the assumption that I have made as to the length of l , the influence of the free electrons, and still more the influence of ionization with increase of temperature, on the specific heat, presents a rather serious question. Thus, to take what is probably the most unfavorable case set forth in the preceding tables, if in Mg $q = 1.5$ and $s = 6.5$ and $\lambda'_0 = 460 R$ and $\gamma = 12\%$, we have, as the heat absorbed by the free electrons in the rise of 1 gm. of Mg from 0°C. to 1°C. , 0.025 cal., while the heat required by the accompanying ionization is 0.124 cal., a total of 0.149 cal., which is rather more than half the total specific heat of Mg at 0°C. It would be easy, however, to choose values of q , s and λ'_0 for Mg which would serve the purpose of this paper while affecting the specific heat less. Moreover, it is possible that l may be greater than I have taken it to be.

Table 17 of my paper in these *Proceedings* for March, 1920, now requires revision, Al, Fe, Mo and Tl going into Section (A); but the general testimony of the table remains unchanged, the *mean* of the last column being now -1.50% for Section (A) and $+2.47\%$ for Section (B).

It remains to be seen whether the theory I am developing can deal successfully with the Peltier effect. A preliminary examination, already made, of this matter is encouraging.

¹ Equipartition of energy, as holding for electrons *within* an atom, cannot be regarded as an established principle.

² *Physic. Rev., Ithaca*, April, 1918 (329).

³ In my previous paper δ_0 had a different meaning.

⁴ *London, Phil. Mag.*, 28, 1914 (692-702).

⁵ *Physic Rev., Ithaca*, May 1919 (374-391).

MOTION ON A SURFACE FOR ANY POSITIONAL FIELD OF FORCE

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1. The first part of the paper presents a study of the geometric properties of the system of trajectories generated by the motion of a particle on any constraining surface (spread of two dimensions) under any positional field of force. The complete characteristic properties are derived.¹ Starting at any point on the surface in a given direction, and with a given speed, a unique trajectory is generated. The complete system of trajectories forms a triply infinite system of curves corresponding uniquely to a given field of force. The five geometric properties stated in section 2 are characteristic of the system of trajectories, and any triply infinite system of curves on a surface possessing these five properties may be considered as generated by the motion of a particle in a unique field of force.